Two-electron Transfer Catalysis of Carbon Monoxide Exchange[1] with a Ligand in Hexacarbonyldi-iron Compounds $[(\mu\text{-RS})_2Fe_2(CO)_6]$

André Darchen,[a]* Hénia Mousser,[a] and Henri Patin[b]

[a] *Laboratoire d'Electrochimie, UA CNRS 439, Université de Rennes I, Campus de Beaulieu, 35042 Rennes Cédex, France*

[b] *Laboratoire de Chimie Organique, UA CNRS 704, Ecole Nationale Supérieure de Chimie, 35700 Rennes Beaulieu, France*

Two-electron reduction of $[(\mu\text{-RS})_2Fe_2(CO)_6]$ (R = alkyl) leads to labile dianionic species which lose CO and decay or, in the presence of a ligand (L) such as $P(OMe)_3$, are involved in a chain reaction affording successively $[(\mu\text{-RS})_2Fe_2(CO)_5L]$ and $[(\mu\text{-RS})_2Fe_2(CO)_4L_2]$.

Since the pioneering work of Rieger *et al.*[2] on electron transfer catalysis (e.t.c.) of carbon monoxide substitution in cluster compounds, many papers have described the use of this new tool in organometallic chemistry for purposes such as ligand exchange,[3] ligand fragmentation,[4] ligand insertion,[5] and isomerization.[6] The e.t.c. of a chemical reaction may be described in terms of two activation steps.[7] The first step has been considered to involve formation of labile paramagnetic species having 17 or 19 electrons in the metallic co-ordination spheres. Chain propagation by electron exchange constitutes the second step. We now report that e.t.c. can also be initiated by a two-electron transfer, without observed paramagnetic species.

Although some examples of two-electron reductions of di-iron complexes have been reported,[8] two-electron transfer catalysis (t.e.t.c.) of a chemical reaction is without precedent. We show in this paper that t.e.t.c. can occur if the following principal conditions for double activation[7] are fulfilled: (i) enhanced reactivity of the intermediate formed after two-electron transfer, and (ii) fast electron exchange to ensure chain propagation.

The readily available dinuclear compounds $[(\mu\text{-RS})_2Fe_2(CO)_6]$ (**1**)[9] are reduced in dimethylformamide (DMF) in a single chemically reversible two-electron step leading to the dianions (**1**$^{2-}$), which are oxidized at less negative potentials (the values of $E_{p_a} - E_{p_c}$ are in the range 0.1—0.2 V). Under N_2 the decomposition of (**1**$^{2-}$) occurs on the voltammetric timescale, as shown by the low intensities of anodic currents of (**1**$^{2-}$) (A1 in Figure 1) and by the presence of peaks corresponding to unidentified electroactive fragments (A2 in Figure 1). However (**1c**$^{2-}$) and (**1d**$^{2-}$), which bear a double-bridging ligand, are more stable (Table 1). In all cases the stabilities of (**1**$^{2-}$) are enhanced by the presence of a CO atmosphere: the anodic currents of (**1**$^{2-}$) increase and, for (**1c**$^{2-}$) and (**1d**$^{2-}$) reach the values expected for a reversible process (Table 1), while the anodic peaks corresponding to unidentified electroactive fragments decrease or disappear (Figure 1). These observations suggest that loss of a CO ligand is a reversible, rate-determining step in the decomposition of (**1**$^{2-}$). The shift towards more negative values of the cathodic peaks under CO atmosphere (Table 1) supports this hypothesis.

Table 1. Electrochemical data for compounds (**1**); E_p and i_p values determined by cyclic voltammetry (DMF; 0.1 M-$Bu_4N^+BF_4^-$; Pt electrode, 20 °C, potential scan rate 0.5 V s^{-1}).

Compound[a]	E_{p_c}[b]/ V *vs.* s.c.e.	i_{p_a}/i_{p_c}[b]	E_{p_c}[c]/ V *vs.* s.c.e.	i_{p_a}/i_{p_c}[c]
(**1a**) S	−1.25		−1.33	0.3
(**1b**) S	−1.21	0.3	−1.30	0.5
(**1b**) A	−1.19	0.25	−1.25	0.4
(**1c**)	−1.17	0.6	−1.20	1.0
(**1d**)	−1.17	0.45	−1.15	0.9

[a] A and S denote *anti*- and *syn*-isomers.[8] The proximity of potential peaks does not allow the study of *anti*/*syn* isomerization. [b] Data obtained under N_2 atmosphere. [c] Data obtained under CO atmosphere.

The cathodic behaviour of compounds (**1**) can be summarized by equations (1)—(3).

$$(\mathbf{1}) + 2e^- \rightleftarrows (\mathbf{1}^{2-}) \qquad (1)$$

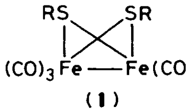
$$(\mathbf{1}^{2-}) \xrightarrow{\text{slow}} [(RS)_2Fe_2(CO)_5]^{2-} + CO \qquad (2)$$

$$[(RS)_2Fe_2(CO)_5]^{2-} \xrightarrow{\text{fast}} \text{decomposition fragments} \qquad (3)$$

When a ligand L [= $P(OMe)_3$] is added to a solution of (**1**) in DMF cyclic voltammetry shows behaviour typical of a ligand substitution catalysed at the surface of the platinum cathode (Figure 1). The cathodic peak C1 of (**1**) decreases while two peaks (C2 and C3), corresponding respectively to the reduction of $[(\mu\text{-RS})_2Fe_2(CO)_5L]$ (**2**) and $[(\mu\text{-RS})_2Fe_2(CO)_4L_2]$ (**3**), appear at more negative potentials. We have checked that $[(\mu\text{-S}[CH_2]_2S\text{-})Fe_2(CO)_5P(OMe)_3]$ (**2c**), obtained independently, is reduced in a single two-electron step (E_{p_c} −1.45 V *vs.* s.c.e. at 0.5 V s^{-1}). This monosubstituted compound (**2c**) is also involved, in the presence of $P(OMe)_3$, in another t.e.t.c. of ligand exchange leading to the disubstituted product $[(\mu\text{-S}[CH_2]_2S\text{-})Fe_2(CO)_4\{P(OMe)_3\}_2]$ (**3c**), identified by its cathodic peak potential (E_{p_c} −1.75 V *vs.* s.c.e. at 0.5 V s^{-1}). Compound (**3c**) is also reducible in a single two-electron step.

Under CO atmosphere the voltammograms of (**2c**) [and (**3c**)] show, during the reverse scan, anodic peaks corresponding to (**1c**$^{2-}$) [and (**1c**$^{2-}$) and (**2c**$^{2-}$)], respectively. Consequently, carbon monoxide replacements by $P(OMe)_3$ are reversible processes occurring in the dianions (**1c**$^{2-}$), (**2c**$^{2-}$), and (**3c**$^{2-}$).

The controlled potential electrolysis of (**1c**) at −1.35 V *vs.* s.c.e., in the presence of $P(OMe)_3$ and under N_2 atmosphere, leads to (**2c**) with a low consumption of electricity [64% yield;



(**1**)

$[(\mu\text{-RS})_2Fe_2(CO)_5L]$ (**2**)

$[(\mu\text{-RS})_2Fe_2(CO)_4L_2]$ (**3**)

a; R = Me
b; R = Et
c; RR = $[CH_2]_2$
d; RR = $[CH_2]_3$

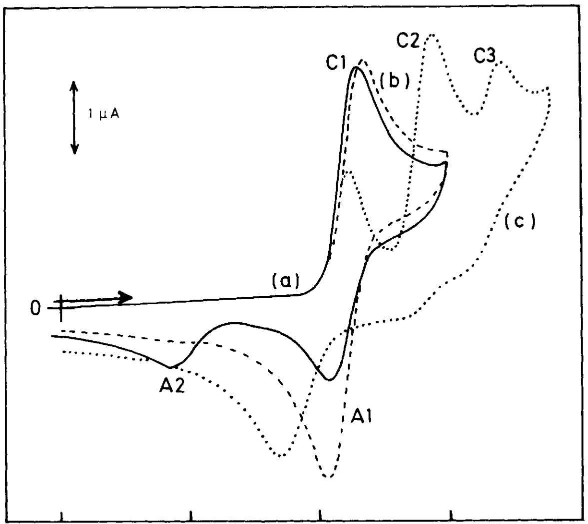


Figure 1. Cyclic voltammetry of compound (**1c**) (2×10^{-3} M) in DMF (0.1 M-$Bu_4N^+BF_4^-$) at a Pt electrode (20 °C; potential scan rate 0.5 V s^{-1}) (a) alone under N_2; (b) alone under CO; (c) under N_2 and in the presence of $P(OMe)_3$ (4×10^{-3} M).

0.1 electron per mol of (**1c**)]. The t.e.t.c. of CO substitutions in compounds (**1**) and (**2**) can then be described by the equations (1), (4), and (5), and (6)—(8), respectively.

$$(\mathbf{1}) + 2e^- \rightleftarrows (\mathbf{1}^{2-}) \qquad (1)$$

$$(\mathbf{1}^{2-}) + L \rightleftarrows (\mathbf{2}^{2-}) + CO \qquad (4)$$

$$(\mathbf{1}) + (\mathbf{2}^{2-}) \rightarrow (\mathbf{1}^{2-}) + (\mathbf{2}) \qquad (5)$$

$$(\mathbf{2}) + 2e^- \rightleftarrows (\mathbf{2}^{2-}) \qquad (6)$$

$$(\mathbf{2}^{2-}) + L \rightleftarrows (\mathbf{3}^{2-}) + CO \qquad (7)$$

$$(\mathbf{2}) + (\mathbf{3}^{2-}) \rightarrow (\mathbf{2}^{2-}) + (\mathbf{3}) \qquad (8)$$

The kinetic analysis[10] of peak currents under N_2 atmosphere reveals that the overall t.e.t.c. of CO substitution in ($\mathbf{1c}^{2-}$) contains a dissociative pathway. This is deduced from the weak dependence of i_p/i_p^0 upon ligand concentration (Figure 2). In contrast, under CO atmosphere the CO ligand substitution in ($\mathbf{1c}^{2-}$) follows an associative mechanism [equation (9)] with a rate constant $k_{ap} = 3.10^2$ l mol^{-1} s^{-1}.

$$(\mathbf{1c}^{2-}) + P(OMe)_3 \xrightarrow{k_{ap}} (\mathbf{2c}^{2-}) + CO \qquad (9)$$

As already mentioned,[9] the two-electron reductions of binuclear di-iron compounds afford diamagnetic dianions in which 18-electron metal centres are formed by cleavage of Fe–Fe bonds. Then if a fast ligand exchange occurs at one metal atom of ($\mathbf{1}^{2-}$), the low redox potential of the couple (**2**)/($\mathbf{2}^{2-}$) allows chain-propagation by two-electron exchange [equation (5)].

However, there remains a question as to whether this apparent t.e.t.c. of ligand substitution is a real two-electron transfer catalysis or a masked classical one-electron transfer catalysis occurring with paramagnetic species generated by the disproportionation reaction (10). It is well known that ligand exchange reactions at paramagnetic metal centres are faster than the same reactions of their diamagnetic precursors.[3,7] However, ligand exchange at the level of ($\mathbf{1}^{\bullet -}$) is unlikely, and the following facts allow the rejection of this hypothesis. Firstly, if ($\mathbf{1}^{\bullet -}$) were produced by reaction (10), the concentration of this species would increase under CO atmosphere, because ($\mathbf{1}^{2-}$) is more stable under these conditions. Thus, in contrast to what is observed, under CO atmosphere the ligand exchange rate should be greater. Secondly, the loss of CO from ($\mathbf{1}^{\bullet -}$) should be the rate-determining step for a ligand exchange reaction occurring by a dissociative process at a 19-electron metal centre. This hypothesis is ruled out by the observation of an associative mechanism under CO atmosphere (Figure 2).

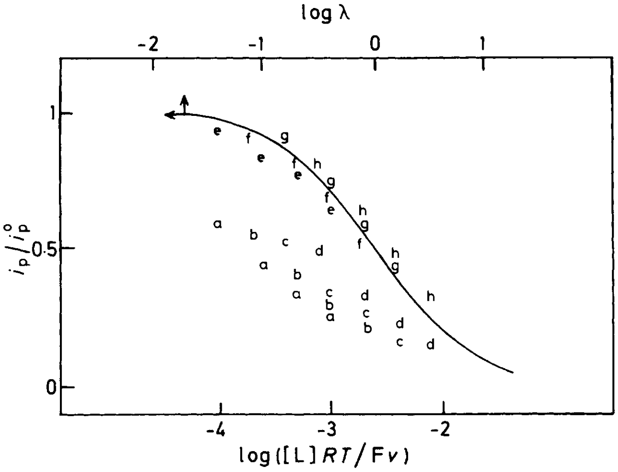


Figure 2. Kinetic analysis of the e.t.c. of CO replacement by $P(OMe)_3$ in compound (**1c**); i_p^0, i_p, [L], and v represent peak currents of (**1c**) alone, (**1c**) in the presence of $P(OMe)_3$, $P(OMe)_3$ ligand concentration, and scanning rate. The non-dimensional parameter λ is $k_{ap}[L]$ RT/Fv. The line is the theoretical curve for ligand exchange by an associative mechanism. The data were obtained under N_2 (a—d) or CO (e—h) for [L] = 2×10^{-3} M (a and e); 4×10^{-3} M (b and f); 8×10^{-3} M (c and g); or 16×10^{-3} M (d and h).

$$(\mathbf{1}^{2-}) + (\mathbf{1}) \rightleftarrows 2\,(\mathbf{1}^{\bullet -}) \qquad (10)$$

The t.e.t.c. reported here is a ligand exchange related to processes occurring at 18-electron metal centres of ($\mathbf{1}^{2-}$). Other associative mechanisms are known when ancillary polyhapto ligands are able, by slippage,[11] to free co-ordination sites in the transition state. In the absence of available ligand the decay of ($\mathbf{1}^{2-}$) probably occurs by stepwise deco-ordination of the surrounding ligands. However, the loss of CO from ($\mathbf{1}^{2-}$) allows a ligand present in solution to co-ordinate. When L = CO, ($\mathbf{1}^{2-}$) is stabilized. When L = $P(OMe)_3$, the dianion ($\mathbf{2}^{2-}$) is formed by the dissociative pathway shown in equations (2) and (11). We suggest that, when CO and $P(OMe)_3$ are both present, an associative process is allowed by the partial deco-ordination of one bridging sulphur ligand.

$$(\mathbf{1}^{2-}) \overset{\text{slow}}{\rightleftarrows} [(RS)_2Fe_2(CO)_5]^{2-} + CO \qquad (2)$$

$$[(RS)_2Fe_2(CO)_5]^{2-} + L \xrightarrow{\text{fast}} \left\{\begin{array}{l}(\mathbf{2}^{2-})\,[L = P(OMe)_3] \\ (\mathbf{1}^{2-})\,(L = CO)\end{array}\right. \qquad (11)$$

Reversible or quasi-reversible two-electron processes have been frequently observed in studies of the electrochemical behaviour of binuclear[12] or trinuclear[13] co-ordination compounds. Providing that two-electron transfer induces bond labilization in these species, one might expect the discovery of new examples of t.e.t.c.†

Dr. C. Amatore (ENS, Paris) is thanked for assistance, and the CNRS for partial financial support.

Received, 9th March 1988; Com. 8/00946E

References

1 For the preceding paper in the series 'Carbon Monoxide Selective Substitution,' see A. Darchen, E. K. Lhadi, and H. Patin, *New J. Chem.*, 1988, **12**, in the press.

2 G. J. Bezems, P. H. Rieger, and S. Visco, *J. Chem. Soc., Chem. Commun.*, 1981, 265.

3 A. Darchen, C. Mahe, and H. Patin, *Nouv. J. Chim.*, 1982, **6**, 539; A. J. Downard, B. H. Robinson, and J. Simpson, *Organometallics*, 1986, **5**, 1132, and refs. therein; H. H. Ohst and J. K. Kochi, *Inorg. Chem.*, 1986, **25**, 2066, and refs. therein; A. Darchen, *J. Chem. Soc., Chem. Commun.*, 1983, 768.

4 E. K. Lhadi, H. Patin, and A. Darchen, *Organometallics*, 1984, **3**, 1128; See also ref. 1.

5 D. L. Reger and E. Mintz, *Organometallics*, 1984, **3**, 1759; M. J. Therien and W. C. Trogler, *J. Am. Chem. Soc.*, 1987, **109**, 5127.

6 J. Courtot-Coupez, M. Gueguen, J. E. Guerchais, F. Y. Petillon, J. Talarmin, and R. Mercier, *J. Organomet. Chem.*, 1986, **312**, 81, and refs. therein.

7 For definition of double activation in e.t.c. and reviews, see M. Chanon and M. L. Tobe, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 1; M. Chanon, *Acc. Chem. Res.*, 1987, **20**, 214.

8 For examples of two-electron reversible reduction of di-iron compounds see R. E. Dessy, R. Kornmann, C. Smith, and R. Haytor, *J. Am. Chem. Soc.*, 1968, **90**, 2001; G. Zotti, R. D. Rieke, and J. S. McKennis, *J. Organomet. Chem.*, 1982, **228**, 281.

9 D. Seyferth, R. S. Henderson, Li-Cheng Song, and G. B. Womack, *J. Organomet. Chem.*, 1985, **292**, 9. A. Lagadec, R. Dabard, B. Misterkiewicz, A. Le Rouzic, and H. Patin, *J. Organomet. Chem.*, 1987, **326**, 381.

10 P. M. Zizelman, C. Amatore, and J. K. Kochi, *J. Am. Chem. Soc.*, 1984, **106**, 3771.

11 F. Basolo, *Inorg. Chim. Acta*, 1985, **100**, 33; J. M. O'Connor and C. P. Casey, *Chem. Rev.*, 1987, **87**, 307.

12 (a) R. E. Dessy, P. M. Weissman, and R. L. Pohl, *J. Am. Chem. Soc.*, 1966, **88**, 5117; (b) D. A. Smith, B. Zhuang, W. E. Newton, J. W. McDonald, and F. A. Schultz, *Inorg. Chem.*, 1987, **26**, 2524; (c) S. G. Shyu, M. Calligaris, G. Nardin, and A. Wojcicki, *J. Am. Chem. Soc.*, 1987, **109**, 3617; (d) Y. Mugnier, P. Reeb, C. Moise, and E. Laviron, *J. Organomet. Chem.*, 1983, **254**, 111; (e) M. Gueguen, J. E. Guerchais, F. Y. Petillon, and J. Talarmin, *J. Chem. Soc., Chem. Commun.*, 1987, 557.

13 R. L. Bedard and L. F. Dahl, *J. Am. Chem. Soc.*, 1986, **108**, 5933.

---

† T.e.t.c. was ruled out in ref. 12e.